(Sensitized) Photolysis of Diazonium Salts as a Mild General Method for the Generation of Aryl Cations. Chemoselectivity of the Singlet and Triplet 4-Substituted Phenyl Cations

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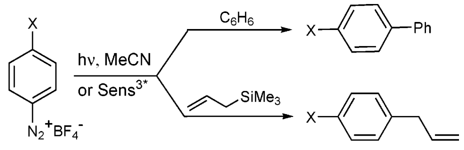

X = NO_2, CH_3CO, CN, Br, H, *t*-Bu, NMe_2

The photolysis of a series of 4-X-benzenediazonium tetrafluoroborates is studied in MeCN. Loss of nitrogen occurs from the singlet excited state with X = H, *t*-Bu, and NMe_2 and leads to the singlet aryl cation. This adds to the solvent yielding the corresponding acetanilides. With other substituents, ISC competes with (X = Br, CN) or overcomes (X = COMe, NO_2) fragmentation and the aryl cation is formed in part or completely in the triplet state. In neat MeCN, this either abstracts hydrogen from the solvent (in most cases inefficiently) or undergoes intersystem crossing to the more stable singlet that reacts as above. In the presence of π nucleophiles (allyltrimethylsilane or benzene), the triplet aryl cation is efficiently trapped giving substituted allylbenzenes and biphenyls, respectively. By triplet sensitization by xanthone, the triplet cation and the products from it are obtained from the whole series considered. The direct or sensitized photodecomposition of diazonium fluoroborates, substituted with both electron-donating and -withdrawing substituents, in the presence of alkenes and arenes offers an access to an alternative arylation procedure.

Introduction

Many synthetic applications of diazonium salts[1,2] involve dediazoniation reactions, which allow C−C bond formation. Typically, these involve radicals generated through single-electron-transfer reduction of the salt,[3] as in the Meerwein arylation of olefins[4] (Scheme 1, path *a*), the Gomberg−Bachmann arylations of aromatics[5] (path *b*), and Pschorr syntheses.[6] Alternatively, aryl−carbon bonds have been formed by the palladium-mediated reactions with aryl boronic acids[7] (path *c*) or with olefins in the Heck synthesis[8] (path *d*).

The alternative (photo)fragmentation to give an aryl cation (path *e*) has been less frequently exploited.[9,10] Such reactions include the Balz−Schiemann fluorination,[11] the synthesis of phenols in an aqueous medium,[12,13] and the synthesis of aryl ethers in alcohols[11a,14,15] but not the more interesting formation of aryl−C bonds.

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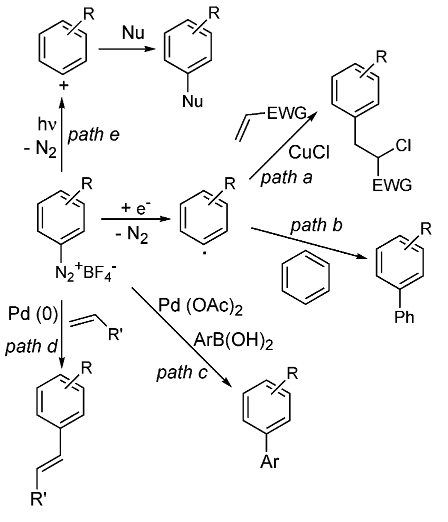
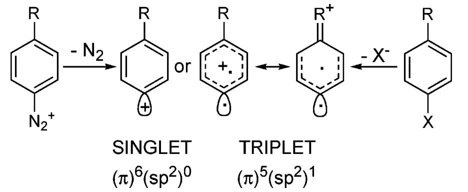
The mechanism of both thermal and photochemical diazonium salt decomposition has been extensively investigated. The thermal decomposition involves either the radical or the cation depending on the medium and the salt used.[16] Water has been considered the best solvent for generating the cation,[13] though the presence of micelles can modify the mechanism.[17] Changing the medium from a water−alcohol mixture[14] to neat alcohol significantly increases the likelihood that a radical will be formed.[15] Among polar nonprotic solvents, acetonitrile[18,19] favors the cations, whereas in DMF[20] or DMSO[18,21] radicals are formed. The mild photochemical decomposition affords a more convenient entry to aryl cations.[22]

SCHEME 1



Apart from diazonium salts, aryl cations have been generated only under particular conditions, viz., the irradiation of bromo - or iodobenzene in a solid argon matrix at 4 K[23] and by solvolysis of perfluoroalkylsulfonic aryl esters[24] and of (trifluoromethanesulfonyl)oxydienynes.[25] To our knowledge, there is no direct evidence for this elusive species in solution.[26] Recently, Steenken and McClelland reported indirect evidence of a phenyl cation by detecting its adduct to 1,3,5-triisopropylbenzene upon laser flash photolysis of 4-methoxyphenyl diazonium tetrafluoroborate.[27]

SCHEME 2



It is important to take into account that aryl cations exist either in the singlet state or in the triplet state (see Scheme 2). Calculations show that the former species is a localized cation with a vacant σ orbital at the dicoordinated carbon atom,[28a] while the triplet state has both diradical and carbene character with single occupancy of that orbital and the charge delocalized on the aromatic ring and on the substituents in the *o*- or *p*-positions.[28,29]

The difference in the electronic distribution is expected to be reflected in the chemoselectivity, but until recently this had little experimental support, due to the difficult access to aryl cations. Our interest in this field stemmed from the finding that *p*-chloro (or fluoro)anilines undergo photoheterolysis and generate the 4-aminophenyl cation in solution in the triplet state (Scheme 2, right-hand side).[30] This intermediate reacted selectively with π nucleophiles[31] in contrast with the unselective reaction with the solvent expected for the singlet cation. Synthetically appealing arylation reactions were developed in this way.

However, photoinduced loss of halide is thermodynamically inaccessible for aromatics not bearing a strong

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electron-donating substituent such as the amino group or a hydroxy(methoxy) group that stabilizes the positive charge formed. A far better leaving group should make diazonium salts suitable candidates for a generally applicable generation of phenyl cations and, we hoped, for C−C bond-forming reactions.

Previously, Schuster et al. showed that substituents affect the result and irradiation of 4-diethylamino or 4-morpholino benzenediazonium salts gave products resulting from the singlet phenyl cation, while the 4-benzoyl derivative underwent radical chain decomposition in 2,2,2-trifluoroethanol (TFE) initiated by triplet phenyl cations.[10]

On the basis of the above, we surmised that a large-scope ionic arylation based upon the photodecomposition of diazonium salts in the presence of C-nucleophiles could be developed provided that (a) thermal processes, whether dediazoniation or thermal addition to the nucleophile, are negligible with respect to photofragmentation in the time scale used; (b) no reagent that may cause reduction of the salt and the formation of the aryl radical is present; and (c) the aryl cation is selectively generated in the triplet state.

Therefore, we embarked on a systematic examination of the photodecomposition of 4-substituted benzenediazonium salts to allow the formation of either singlet or triplet phenyl cations to be determined, and possibly directed, and the scope of the arylation by this pathway to be ascertained. In the following we report the photodecomposition of a series of diazonium tetrafluoroborates **1a**−**g** in neat MeCN and in the presence of representative π nucleophiles.[32]

Results

Seven 4-substituted benzenediazonium tetrafluoroborates were selected for a study ranging from those bearing electron-withdrawing groups (X = NO_2, **1a**; X = $COCH_3$, **1b**; X = CN, **1c**; X = Br, **1d**) to the parent benzenediazonium salt (X = H, **1e**) to those bearing electron-donating substituents (X = *t*-Bu, **1f**; X = NMe_2, **1g**). Acetonitrile (0.1% water content) was chosen as the reaction medium as a polar solvent, which effectively dissolved all of the salts and reagents used (see Discussion for further details). To assess the contribution of thermal decomposition in the experiments, blank tests were routinely carried out under the irradiation conditions by covering the test tubes with aluminum foil. Only in the case of **1a** was there a slight consumption (<10%) of the salt during the time required for complete photodecomposition. Photolyses were carried out in a multilamp apparatus by means of lamps with the maximum of emission at 310 or 360 nm. Irradiation at 310 nm was convenient for the direct photodegradation of the salts (c = 0.05 M), though 360 nm could be used equally well for **1a**, **1b**, and **1g**. In the sensitized experiments with xanthone (or benzophenone), 360 nm lamps were used (310 nm in the case of **1g**). In these experiments, the diazonium salt concentration was in some cases decreased (down to 0.01 M) in order to ensure a >95% absorption by the sensitizer (see below and Experimental Section).

SCHEME 3

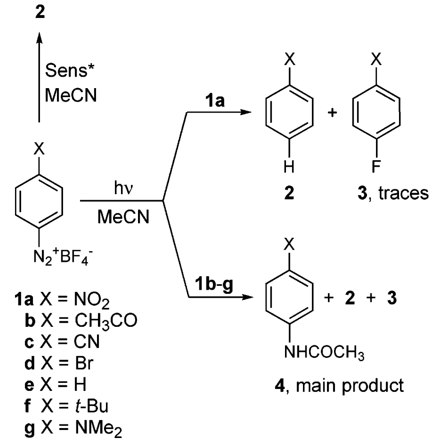
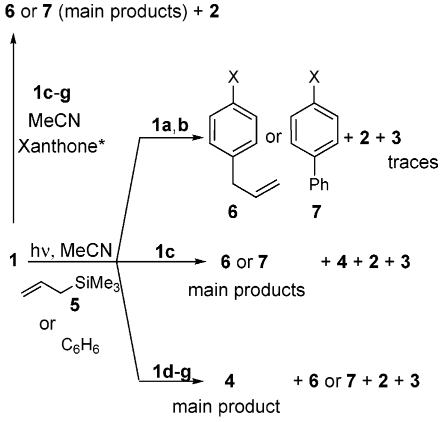


TABLE 1. Products from the Irradiation of Diazonium Fluoroborates 1 in MeCN

		product yield %[a]					
		direct irradiation			sensitized irradiation		
salt	X	**2**	**3**	**4**	**2**	**3**	**4**
1a	NO_2	24					
1b	CH_3CO	29		37	57		
1c	CN	5	7	69	49		
1d	Br	3		41	67		
1e	H	*b*	*b*	76	*b*	*b*	5
1f	*t*-Bu		4	86	68		
1g	NMe_2	2		68	29		

[a] GC yields; no figure is reported when below 0.5%. [b] Not determined.

SCHEME 4



Irradiation of **1a**−**g** in MeCN at 20 °C caused effective photodediazoniation (total conversion required 3 h for **1a** and 1 h for the other salts). Photolysis of nitroderivative **1a** yielded nitrobenzene **2a** in a modest yield as the only product (Scheme 3 and Table 1).

Hydrodediazoniation giving **2b** was observed also in the case of **1b** (29% acetophenone), but acetanilide **4b** was formed in a larger amount (37%) (see Scheme 3). In view of the difference with **1a**, photosensitization by aromatic ketones was tested. With xanthone (absorbing > 95% of the light), reduction was the exclusive path (57% of **2b** formed). Cyanophenyl diazonium salt **1c** gave acetanilide **4c** as by far the main product (69%) accompanied by small amounts of benzonitrile **2c** and 4-fluorobenzonitrile **3c** (5 and 7%, respectively). Again,

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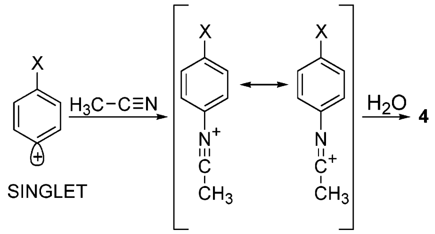
[32] Preliminary communication of part of these data: Milanesi, S.; Fagnoni, M.; Albini A. *Chem. Commun.* **2003**, 216−217.

SCHEME 5



xanthone sensitization made reduction to benzonitrile **2c** the exclusive path.

The same trend as with **1c** was followed in the photodegradation of the remaining salts **1d**−**g**. These gave acetanilides **4d**−**g**, with trace amounts of **2** and **3** by direct irradiation, while substitution of the diazo group by a hydrogen predominated upon xanthone or, with somewhat lower efficiency, benzophenone sensitization.

The reaction was then explored in the presence of two π nucleophiles, viz., allyltrimethylsilane (**5**) (1 M) and benzene (3.75 M). Since diazonium salts, particularly the most electrophilic derivatives, are known to form complexes with aromatic donors,[33] the UV spectra in the presence of the above additives were tested. No significant variation of the UV spectra was observed in the case of salts **1b** and **1e**−**g**, while a modest variation took place with **1d**. A more conspicuous variation occurred in the case of **1c**, as well as with **1a**, but then only with **5** (see Supporting Information).

With these additives, direct irradiation of **1a** gave *p*-allylnitrobenzene (**6a**) and *p*-nitrobiphenyl (**7a**), respectively, both in >50% yield, while the yield of **2a** was reduced to 5% (in fact, 87% **7a** was achieved with 7.5 M benzene, despite the fact that **1a** was not completely dissolved in the initial reaction mixture) (Scheme 4 and Table 2). Likewise with **1b**, the arylation products **6b** and **7b** were formed at the expense of acetanilide **4b** (suppressed) and acetophenone **2b** (decreased).

With the cyanoderivative **1c**, arylation to **6c** and **7c** occurred in ca. 50% yield, with some reduction in the amount of **4c**, **2c**, and **3c** with respect to the experiments in neat solvent. Triplet sensitization was effective and increased the formation of aryl−carbon bond, particularly for the case of 4-cyanobiphenyl (**7c**) in the presence of benzene (84% yield compared to 44% by direct irradiation, see Table 2). Similar to the experiment in neat solvent, no acetanilide **4c** was formed by photosensitization.

Arylated derivatives **6d** and **7d** were obtained in modest yields (<25%) by direct irradiation of **1d**, and the presence of the nucleophiles did not decrease the formation of the acetanilide **4d** in this case. Upon sensitization, **4d** was not formed, and the yield of the 4-allyl- and phenyl bromobenzenes (accompanied by ca. 30% **2d**) increased. Likewise, **1e** gave **6e** and **7e** only by xanthone sensitization (see Table 2).

TABLE 2. Products from the Irradiation of Diazonium Fluoroborates 1 in the Presence of π Nucleophiles

			product yield %[a]							
			direct irradiation				sensitized irradiation			
salt	X	nucleophile[b]	**6** (or **7**)	**2**	**3**	**4**	**6** (or **7**)	**2**	**3**	**4**
1a	NO_2	**5**	51	5						
1a	NO_2	C_6H_6	74, 87[c]	6						
1b	CH_3CO	**5**	50	14						
1b	CH_3CO	C_6H_6	40	18						
1c	CN	**5**	47	5	1	7	48	6		
1c	CN	C_6H_6	44	4	9	35	84	10		
1d	Br	**5**	25	2	<2	41	58	29		
1d	Br	C_6H_6	15	7		62	54	26		
1e	H	**5**	5	*d*	*d*	81	47	*d*	*d*	5
1e	H	C_6H_6	9	*d*	*d*	60	32	*d*	*d*	9
1f	*t*-Bu	**5**	2	4		89	48	34	6	
1f	*t*-Bu	C_6H_6	12	12		70	17	61		
1g	NMe_2	**5**	2	3		87	55	13		
1g	NMe_2	C_6H_6	25	2		63	41	2		

[a] Isolated yields for compounds **6** and **7**; GC yields in the other cases; no figure is reported when below 0.5%. [b] Reaction in the presence of either 1 M **5** or 3.75 M benzene. [c] Reaction in the presence of 7.5 M benzene. [d] Not determined.

TABLE 3. Quantum Yield of Photodecomposition of Diazonium Fluoroborates 1a−g in MeCN[34]

diazonium salt	quantum yield
1a, X = NO_2	<0.1
1b, X = $COCH_3$	0.21
1c, X = CN	0.35
1d, X = Br	0.34
1e, X = H	0.50
1f, X = *t*-But	0.38
1g, X = NMe_2	0.52

4-*tert*-Butyldiphenyl (**7f**) was formed in a low yield, both upon direct and sensitized irradiation (with 61% **2f** in the latter case), while 4-*tert*-butylbenzene (**6f**) was the main product by sensitization. Acetanilide **4g** remained the main product from **1g** by direct irradiation in the presence of the above nucleophiles (87 and 63% yields, respectively), along with 2% **6g** and 25% **7g**. However, the yields of the last compounds increased to 55 and 41%, respectively, upon sensitization.

Quantum Yield Measurement. Quantum yields of decomposition of compounds **1a**−**g** were determined by photolysis of the salts in MeCN at 313 nm. The extent of decomposition (10−20%) was determined by UV absorbance of the azo derivative formed after coupling with *β*-naphthol (see Experimental Section). The results are reported in Table 3.

Quantum yields were moderately affected by changing the substituent X and in every case did not exceed unity. Strong electron-withdrawing substituents such as the nitro group and the acetyl group increased the photostability of the salts to some extent, especially in the case of **1a** (Φ < 0.1). The quantum yield value was slightly higher in the case of salts **1a**−**c** when measured at a more extensive decomposition.

Discussion

Choice of Solvent. The aim of this work is to explore the conditions for the addition of phenyl cations to π nucleophiles. The choice of solvent depends on the ability to dissolve both the precursor diazonium salts and benzene and allyltrimethylsilane, as well as to favor the

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heterolytic rather than the homolytic decomposition of the salt. Water and alcohols (e.g., MeOH or a fluorinated alcohol such as TFE) are able to stabilize the charged intermediates formed[22] but have some drawbacks. As an example, water does not dissolve most organic reagents and may compete as a nucleophile for the cation. The high hydrogen donor ability of methanol can lead to a radical chain upon photolysis of diazonium salts, particularly of the most electrophilic ones. As an example, 4-nitrobenzenediazonium chloride was suggested to give the aryl cation in water but radicalic species in EtOH or MeOH.[35] Furthermore, even the less electrophilic 4-methylbenzenediazonium salt underwent free-radical reduction upon pulse radiolysis in MeOH.[36] In TFE, the formation of aryl radicals is less likely than in unfluorinated alcohols but cannot be excluded.[10] The excellent ion stabilization by TFE[37] is in part counterbalanced by its high price and the tendency to form aromatic fluorides by fluoride transfer to the aryl cation intermediate.[9b] Moreover, both alcohols and water may compete as nucleophiles and give phenol[13,38] and aryl ethers.[15] Acetonitrile was chosen as a reasonably polar solvent and a poor hydrogen donor. Benzene and allyltrimethylsilane were chosen as nucleophiles because they have been previously shown to give clean reactions and high yields in the trapping of (triplet) 4-aminophenyl cation.[30]

Mechanism and Scope of the Reaction. The reactions were carried out at a relatively low temperature (ca. 20 °C), and both the solvent and the diazonium salts were freshly purified in order to avoid impurity-induced photodecomposition side reactions. Under these conditions, arylallylazo and diarylazo compounds, which may be expected from the thermal reaction between **1a**−**g** and **5** and benzene, respectively, were not formed during the time required for decomposition. Mayr[39a] and others[40] introduced parameters for the electrophilicity of diazonium salts and compared such values with the nucleophilicity of olefins and aromatics. This allows the prediction of which diazonium salt is able to attack a specific nucleophile under thermal conditions.[39a] Accordingly, benzene is not expected to react with any of the salts used in this work, while azo-coupling involving **5**[39] is expected to occur with **1a**,**c**[41] but only marginally with **1d**. The analysis of the photoproducts evidences that in all of the cases, including the best electrophile of the series, **1a**, photodediazoniation occurs faster than thermal azo-coupling. Thus, arylation via photodecomposition of diazonium salts can be extended, at least in principle, to several nucleophilic olefins and (hetero)aromatics, provided that the competing thermal coupling is sufficiently slow at room temperature (or below).

All of the photoproducts obtained can be rationalized as arising from aryl cations, and the dependence of the chemistry occurring on the structure of the 4-substituted phenyl cation is the key point of this work. Calculations show that π-donating substituents (F, OH, NH_2) stabilize the triplet state much more than the singlet state.[28a] Actually, only the 4-aminophenyl cation has the triplet state as the lowest state, while in the 4-hydroxy derivative the two spin states are close in energy. In all the other cases, the singlet is the lowest state.[28] Due to the singlet multiplicity of the diazonium salt ground state and the energy order of the aryl cations, in thermal decomposition only the singlet aryl cation chemistry is expected and indeed observed.[13−21] This is not necessarily the case for the photodecomposition.

Direct irradiation of **1b**−**g** in neat acetonitrile leads mainly to the corresponding acetanilides. These are formed by reaction of the photogenerated aryl cation with the solvent to yield a nitrilium ion, which adds moisture present in the solvent, in a way analogous to the Ritter reaction[42] (see Scheme 5).

This has not been previously reported in photolyses but has been in the thermal decomposition (at 40 °C) of benzenediazonium tetrafluoroborate in acetonitrile.[19,43] The reaction is safely attributed to the attack by the singlet aryl cation to a poor nucleophile such as acetonitrile. The overall yield of formation of product **4** is high from **1c**−**g**. In some cases, a small amount of fluorinated compounds **3** is detected, reasonably via reaction with the fluoroborate counterion, as established in related cases.[9b] The presence of nitro or acetyl substituents changes significantly the photoreactivity, and the acetanilide is accompanied (in the case of **1b**) or substituted (in the case of **1a**) by the hydrodediazoniated derivatives **2a**,**b**. Photoreduction to **2c**−**g** is a minor path for the other salts but becomes the main reaction upon sensitization by aromatic ketones. The interaction between triplet excited sensitizers and the diazonium salts has been studied by two independent groups. The first suggested an electron-transfer process causing reduction of the diazonium salt and formation of an aryl radical.[44] Thus, sensitization by aromatic ketones in acetonitrile led to the corresponding aromatic hydrocarbons.[45] However, Scaiano and co-workers demonstrated that energy transfer occurs with high-energy triplet sensitizers such as benzophenone or xanthone, while electron transfer occurs with low-energy sensitizers such as anthracene or pyrene.[46]

Under our conditions, photoreduction is the only process in the presence of xanthone. The result is completely different from direct irradiation and is attributed to the triplet aryl cation. This abstracts a hydrogen from the medium, forming a radical cation that in turn is reduced to the hydrodediazoniated product **2**

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[34] Quantum yield values have been redetermined with respect to the data in ref 32.

[35] Lee, W. E.; Calvert, J. G.; Malmberg, E. W. *J. Am. Chem. Soc.* **1961**, *83*, 1928−1934.

[36] Packer, J. E.; House, D. B.; Rasburn, E. J. *J. Chem. Soc. B* **1971**, 1574−1578.

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[40] Perez, P. *J. Org. Chem.* **2003**, *68*, 5886−5889.

[41] No data on **1b** are reported in ref 39a, but we expect that the behavior of this salt is similar to that of **1a** and **1c**.

[42] Ho, T.-L.; Chein, R.-J. *J. Org. Chem.* **2004**, *69*, 591−592.

[43] Analoguous benzanilides were obtained from the irradiation of imidate esters through the intermediacy of an *N*-arylbenzonitrilium ion. See: Ruane, P. H.; Ahmed, A. R.; McClelland, R. A. *J. Chem. Soc., Perkin Trans. 2* **2002**, 312−317.

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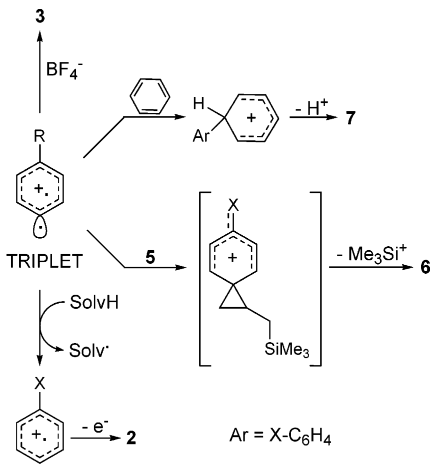
[45] Timpe, H.-J.; Kronfeld, K.-P.; Schiller, M. *J. Photochem. Photobiol. A* **1991**, *62*, 245−259.

[46] Scaiano, J. C.; Kim-Thuan, N. *Can. J. Chem.* **1982**, *60*, 2286−2291.

SCHEME 6



(Scheme 6). This path has been demonstrated for triplet 4-aminophenyl cation generated in MeCN by photolysis of 4-chloroanilines.[30]

Alternatively, aryl cations in the triplet state are trapped by **5** (forming products **6**) or benzene (yielding products **7**) (Scheme 6). In the first case, a phenonium ion can be envisaged as the intermediate[31b,47] and gives **6** via elimination of the good positive leaving group trimethylsilyl cation. Analogously, addition onto benzene gives a cyclohexadienyl cation that deprotonates to **7**. Fast elimination of a proton or a trimethylsilyl group from the adduct cation avoids competing paths (e.g., polymerization for olefins).

Efficient trapping requires a high concentration of the π nucleophiles (1 M for **5** and 3.75 M for benzene) due to the short lifetime of the intermediate.

Under our conditions, some complexation of most of the diazonium salts **1** and π nucleophiles occurs, as indicated by small shifts of the absorption spectra, more apparent in the case of **1a**,**c** (see the spectra at two different concentrations in Supporting Information). Since the effect is varied and at any rate moderate, while the chemistry observed is uniform over the series, we conclude that excitation of EDA complexes has no major role. Thus, in the present case, the EDA route to aryl radicals observed by Kochi[33] with salts that are more easily reduced than the present ones is not important.

There is indication in the literature that the photodecomposition of diazonium salts can occur with a quantum yield significantly greater than unity. This has been observed when the salt is strongly electrophilic and the medium is a good hydrogen donor (e.g., an alcohol). As an example, Kochi reported quantum yields ranging from 1.5 to 11 in the irradiation of 3,5-dinitro-, 2,4,6-trichloro-, and 3,5-difluorobenzenediazonium salts in acetonitrile via an excited complex in the presence of aromatic hydrocarbons.[33c] Furthermore, a quantum yield up to eight has been reported in the photodecomposition of a 4-methylbenzenediazonium derivative in aqueous solution when MeOH is added to the solution.[36] A radical chain reaction initiated by hydrogen abstraction by the aryl cation intermediate from the solvent (SolvH = MeOH[15a,b] or TFE[10]) has been envisaged (Scheme 7).

Initially, hydrogen abstraction leads to the formation of $\text{Solv}^{\bullet}$ and the radical cation of the hydrodediazoniated product (eq a). In solution, easily oxidized radicals such as $^{\bullet}CH_2OH$ are known to reduce diazonium salts to the corresponding radicals[45,48] (eq b). A further hydrogen abstraction gives rise to the reduced aromatic (ArH) and radical $\text{Solv}^{\bullet}$ is regenerated and continues the chain (eq c). The termination of the chain involves a radical–radical cation combination (eq d).

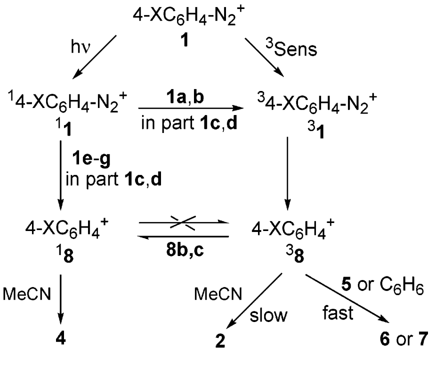
SCHEME 7

$$\text{a)}\quad {}^3Ar^+ + \text{SolvH} \longrightarrow ArH^{+\cdot} + \text{Solv}^{\cdot}$$
$$\text{b)}\quad \text{Solv}^{\cdot} + ArN_2^+ \longrightarrow ArN_2^{\cdot} + \text{Solv}^+$$
$$\text{c)}\quad ArN_2^{\cdot} + \text{SolvH} \longrightarrow ArH + \text{Solv}^{\cdot} + N_2$$
$$\text{d)}\quad \text{Solv}^{\cdot} + ArH^{+\cdot} \longrightarrow ArH + \text{Solv}^+$$

In the present case (SolvH = MeCN), the decomposition quantum yields of **1a**–**g** ($\Phi < 1$ in all cases) support that no radical chain process is involved, as indicated also by the fact that addition of the nucleophiles has a minimal effect on the reaction times (except for **1a**). The difference is that with a poor electron donor such as $^{\bullet}CH_2CN$, step *b* (Scheme 7) is much less efficient than with $^{\bullet}CR_2OH$, at least with moderate electron acceptors such as the present diazonium salts. Photodecomposition in acetonitrile is generally less efficient than reported in hexafluoro 2-propanol (Φ ca. 0.9 for all of the salts investigated)[27] but follows the same trend, with strong electron-withdrawing substituents decreasing the photoreactivity.[12]

On the basis of the above, a comprehensive mechanism for the photodegradation of diazonium salts is outlined in Scheme 8. Irradiation of compounds **1a**–**g** leads to a population of the singlet excited state (^{1}**1**). The nature of the substituents present on the aromatic ring directs the following steps of the reaction. In the case of **1e**–**g**, direct dediazoniation affords singlet aryl cations ^{1}**8** (Scheme 8) and acetanilides **4** by addition to acetonitrile, a n nucleophile. With the other salts, intersystem crossing (ISC) from ^{1}**1** to the corresponding triplet (^{3}**1**) takes place in part (for salts **1c**,**d**) or completely (for **1a** and **1b**) before fragmentation.

SCHEME 8



Sens = Benzophenone, xanthone

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[47] B3LYP calculations have shown that the analogous 4-aminophenyl cation adds to ethylene to form a triplet phenonium; the corresponding singlet is much more stabilized, and intersystem crossing back to the singlet surface reasonably occurs at this configuration. See ref 30a.

[48] Scaiano, J., C.; Kim-Thuan, N. *J. Photochem.* **1983**, *21*, 167–170.

Cleavage of the triplet yields the triplet aryl cation ^{3}**8**. In neat solvent, hydrogen transfer from acetonitrile to ^{3}**8** yields reduced derivatives **2** (Scheme 6). Since MeCN is a poor hydrogen donor, the process is slow and equilibration of the aryl cation to the more stable singlet state is competitive with ^{3}**8b** and ^{3}**8c**. As a result, a certain amount of compounds **4b** and **4c** is formed in these cases. When π nucleophiles are added, there is no change in the product distribution for **1e**−**g**, since singlet aryl cations are formed and then trapped by the solvent, with only small amounts of compounds **6** and **7**. Other substituents favor ISC to ^{3}**1** and enhance the triplet cation chemistry. This is evidenced by addition onto π nucleophiles, a much faster process than hydrogen abstraction from acetonitrile, especially when a large amount of the nucleophile is present. The bromine atom in **1d** and the cyano group in **1c** exert such an effect. With a nitro group (**1a**) or an acetyl group (**1b**), ISC is faster than cleavage of ^{1}**1** and the triplet aryl cation is exclusively formed as revealed by the efficient reaction with benzene and **5**; however, in neat solvent, ISC from ^{3}**8** to ^{1}**8** occurs to some extent with **1b** and gives some **4b** along with the hydrogen abstraction product **2b**.

However, access to ^{3}**8** can be made general by sensitization by aromatic ketones, and under these conditions reduction to **2** in neat solvent and arylation of benzene and of **5** in the presence of such additives are the predominant processes with *all* of the diazonium salts considered.

Conclusion

The photodecomposition of a series of benzenediazonium salts with substituents of various electronic nature at position 4 is a convenient method for the generation of aryl cations. This widens the scope of phenyl cation photogeneration previously limited to the highly stabilized 4-aminophenyl or 4-hydroxy(methoxy)phenyl cation obtained by photolysis of chloroanilines[30,31] and chlorophenols(anisoles),[49] respectively. The nature of the substituents and the choice of direct or sensitized irradiation direct the formation of phenyl cations in either spin state, each of which shows a distinctive chemistry. The triplet ion in every case can be obtained by photosensitization.

The reaction of triplet aryl cations with π nucleophiles offers a new aryl S_N1 substitution with formation of an aryl−carbon bond under mild, metal-free conditions. This method can be applied to the synthesis of biaryls (a very important topic at the moment, due to the wide variety of applications of the products formed)[6] and can be considered both an ionic analogue of the Gomberg reaction and a possible alternative to the palladium-mediated Suzuki coupling. Furthermore, the reactions between aryl cations and **5** offer a general method for the allylation of aromatics, up to now obtained only through aryl radical[50] and metal-mediated reactions,[51] which have a different scope. The general application of the S_N1 reactions via photogenerated aryl cations is currently under investigation in our laboratory.

Experimental Section

NMR spectra were recorded on a 300 MHz spectrometer. Structure attributions were made on the basis of analytical data and of ^{1}H and ^{13}C NMR (chemical shifts are reported in parts per million downfield from TMS). The photochemical reactions were performed at 20 °C in quartz tubes by using a nitrogen-purged solution and a multilamp reactor fitted with six 15 W phosphor-coated lamps (maximum emission of 310 or 360 nm) for the irradiation.

Diazonium salts were prepared by a known procedure[10] and purified by dissolving in acetonitrile or acetone and precipitation by adding Et_2O. Authentic samples of the acetanilides **4a**−**g** were prepared from the corresponding anilines, crystallized from ethanol, and used as standards. Acetonitrile was used as received, and the water content was determined by Karl−Fischer titration.[52]

The reaction course was followed by monitoring the disappearance of the salt up to the point when no color change occurred upon addition of some drops of an aqueous basic solution of β-naphthol. Diluted aqueous $NaHCO_3$ was added to the irradiated solutions, and the product distribution was monitored by GC analysis after extraction with diethyl ether. Preparative experiments involved concentration in vacuo of the photolyzed solution followed by chromatographic separation on silica gel.

Quantum Yield. Quantum yield measurements were made on an optical bench fitted with a focalized high-pressure mercury arc and an interference filter (transmission maximum of 313 nm). The consumption of the salt was determined by monitoring the absorption of the azo derivative formed upon treatment with a few drops of an aqueous basic solution of β-naphthol.

Thermal Stability of Salts 1. All irradiations reported below were repeated under the same conditions with the tube covered by aluminum foil. Diazonium salts **1** remained practically undecomposed in most cases (the maximal consumption observed was in the case of **1a**, <10%).

Irradiation of Diazonium Salts 1. General Procedure. A 0.05 M solution of **1** in MeCN (prepared under shaded light) was irradiated at 310 nm at 20 °C up to complete consumption of the salt; the same experiments were carried out in the presence of either allyltrimethylsilane (1 M) or benzene (3.75 or 7.5 M). In sensitized irradiation experiments, diazonium salts **1** ($(1-5) \times 10^{-2}$ M) and xanthone ($(4-6) \times 10^{-2}$ M) were dissolved in MeCN and irradiated at 360 nm (310 for the case of **1g**, see below). Benzophenone (5×10^{-2} M) was also used in the place of xanthone in the photodegradation reactions of salts **1e**,**f** giving a lower yield of products **6** and **7**. In the synthesis of compounds **6g** and **7g**, the radiation was filtered by means of a 1.5×10^{-2} M solution of *o*-nitroaniline in order to prevent direct absorption by the diazonium salt.

4-(2-Propenyl)-nitrobenzene (6a). From 355 mg (1.5 mmol, 5×10^{-2} M) of **1a** and 4.7 mL (30 mmol, 1 M) of **5** in 30 mL of MeCN irradiated at 310 nm. After column chromatography (C_6H_{12}/EtAc 98/2), 124 mg of the title compound **6a** (oil) was isolated (51% yield). Spectroscopic data were in accordance with the literature.[50]

4-Nitrobiphenyl (7a). From 355 mg (1.5 mmol, 5×10^{-2} M) of **1a** and 10 mL (112.6 mmol, 3.75 M) of benzene in 20 mL of MeCN irradiated at 310 nm. After column chromatography (C_6H_{12}/EtAc 98/2), 218 mg of the title compound **7a**

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[52] Use of acetonitrile with a higher water content (up to some percent) did not affect the overall arylation yields in sensitized experiments.

(colorless solid) was isolated (74% yield). Mp 112−114 °C (lit.[53] 112−113 °C). Spectroscopic data were in accordance with the literature.[54]

4-(2-Propenyl)-acetophenone (6b). From 351 mg (1.5 mmol, 5×10^{-2} M) of **1b** and 4.7 mL (30 mmol, 1 M) of **5** in 30 mL of MeCN irradiated at 310 nm. After column chromatography (C_6H_{12}/EtAc 95/5), 120 mg of the title compound **6b** (oil) was isolated (50% yield). Spectroscopic data were in accordance with the literature.[55]

4-Phenylacetophenone (7b). From 351 mg (1.5 mmol, 5×10^{-2} M) of **1b** and 10 mL (112.6 mmol, 3.75 M) of benzene in 20 mL of MeCN irradiated at 310 nm. After column chromatography (C_6H_{12}/EtAc 98/2), 118 mg of the title compound **7b** (colorless solid) was isolated (40% yield). Mp 116−118 °C (lit.[56] 119−120 °C). Spectroscopic data were in accordance with the literature.[57]

4-(2-Propenyl)-benzonitrile (6c). From 325 mg (1.5 mmol, 5×10^{-2} M) of **1c**, 4.7 mL (30 mmol, 1 M) of **5**, and 235 mg (1.2 mmol, 4×10^{-2} M) of xanthone in 30 mL of MeCN irradiated at 366 nm. After column chromatography (C_6H_{12}/EtAc 99/1), 102 mg of the title compound **6c** (oil) was isolated (48% yield). Spectroscopic data were in accordance with the literature.[58]

4-Phenylbenzonitrile (7c). From 325 mg (1.5 mmol, 5×10^{-2} M) of **1c**, and 10 mL (112.6 mmol, 3.75 M) of benzene, and 235 mg (1.2 mmol, 4×10^{-2} M) of xanthone in 20 mL of MeCN irradiated at 366 nm. After column chromatography (C_6H_{12}/EtAc 97.5/2.5), 225 mg of the title compound **7c** (colorless solid) was isolated (84% yield). Mp 85−87 °C (lit.[59] 86−87 °C). Spectroscopic data were in accordance with the literature.[54]

4-(2-Propenyl)-bromobenzene (6d). From 162 mg (0.6 mmol, 2×10^{-2} M) of **1d**, 4.7 mL (30 mmol, 1 M) of **5**, and 235 mg (1.2 mmol, 4×10^{-2} M) of xanthone in 30 mL of MeCN irradiated at 366 nm. After column chromatography (C_6H_{12}/EtAc 95/5), 68 mg of the title compound **6d** (oil) was isolated (57.5% yield). Spectroscopic data were in accordance with the literature.[50]

4-Bromobiphenyl (7d). From 162 mg (0.6 mmol, 2×10^{-2} M) of **1d**, 10 mL (112.6 mmol, 3.75 M) of benzene, and 235 mg (1.2 mmol, 4×10^{-2} M) of xanthone in 20 mL of MeCN irradiated at 366 nm. After column chromatography (neat C_6H_{12}), 76 mg of the title compound **7d** (colorless solid) was isolated (54% yield). Mp 89−91 °C (lit.[53] 89−90 °C). Spectroscopic data were in accordance with the literature.[60]

3-Phenyl-1-propene (6e). From 290 mg (1.5 mmol, 5×10^{-2} M) of **1e**, 4.7 mL (30 mmol, 1 M) of **5**, and 235 mg (1.2 mmol, 4×10^{-2} M) of xanthone in 30 mL of MeCN irradiated at 366 nm. After column chromatography (C_6H_{12}/EtAc 97/3), 83 mg of the title compound **6e** (oil) was isolated (47% yield). Spectroscopic data were in accordance with a commercial sample (Fluka).

Biphenyl (7e). From 290 mg (1.5 mmol, 5×10^{-2} M) of **1e**, 10 mL (112.6 mmol, 3.75 M) of benzene, and 235 mg (1.2 mmol, 4×10^{-2} M) of xanthone in 20 mL of MeCN irradiated at 366 nm. After column chromatography (neat C_6H_{12}), 74 mg of the title compound **7e** (colorless solid) was isolated (32% yield). Mp 66−68 °C (Fluka catalog 68−70 °C). Spectroscopic data were in accordance with a commercial sample (Fluka).

4-(2-Propenyl)-*tert*-butylbenzene (6f). From 372 mg (1.5 mmol, 5×10^{-2} M) of **1f**, 4.7 mL (30 mmol, 1 M) of **5**, and 235 mg (1.2 mmol, 4×10^{-2} M) of xanthone in 30 mL of MeCN irradiated at 366 nm. After column chromatography (neat C_6H_{12}), 125 mg of the title compound **6f** (oil) was isolated (48% yield). Spectroscopic data were in accordance with the literature.[61]

4-*tert*-Butylbiphenyl (7f). From 372 mg (1.5 mmol, 5×10^{-2} M) of **1f**, 10 mL (112.6 mmol, 3.75 M) of benzene, and 235 mg (1.2 mmol, 4×10^{-2} M) of xanthone in 20 mL of MeCN irradiated at 366 nm. After column chromatography (neat C_6H_{12}), 53 mg of the title compound **7f** (colorless solid) was isolated (17% yield). mp 49−51°C (lit.[62] 51−52°C). Spectroscopic data were in accordance with the literature.[63]

4-(2-Propenyl)-*N,N*-dimethylaniline (6g).[64] From 140 mg (0.6 mmol, 10^{-2} M) of **1g**, 9.4 mL (60 mmol, 1 M) of **5**, and 470 mg (2.4 mmol, 4×10^{-2} M) of xanthone in 60 mL of MeCN irradiated at 310 nm. After column chromatography (C_6H_{12}/EtAc 98/2), 53 mg of the title compound **6g** (oil) was isolated (55% yield). Data for **6g**: ^{1}H NMR (CDCl$_3$) δ 6.7−7.05 (AA′BB′, 4 H), 5.9 (m, 1 H), 4.95−5.1 (m, 2 H), 3.3 (d, ^3J (H,H) = 6.5 Hz, 2 H), 2.95 (s, 6 H); IR (neat) ν (cm^{-1}) 2924, 1638, 1345, 836.

4-*N,N*-Dimethylaminobiphenyl (7g). From 140 mg (0.6 mmol, 10^{-2} M) of **1g**, 20 mL (112.6 mmol, 3.75 M) of benzene, and 470 mg (2.4 mmol, 4×10^{-2} M) of xanthone in 40 mL of MeCN irradiated at 310 nm. After column chromatography (C_6H_{12}/EtAc 98/2), 48 mg of the title compound **7g** (colorless solid) were isolated (41% yield). Mp 118−120 °C (lit.[65] 121−122 °C). Data for **7g**: ^{1}H NMR (CDCl$_3$) δ 7.25−7.55 (m, 5 H), 6.82−7.5 (AA′BB′, 4 H), 3.02 (s, 6 H); IR (neat) ν (cm^{-1}) 3051, 1353, 820.

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Supporting Information Available: UV spectra of salts **1a**−**g** in the presence of both benzene (1.5 and 3.75 M) and **5** (0.5 and 1 M). This material is available free of charge via the Internet at http://pubs.acs.org.

JO048413W

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